

СИНТЕЗ И СТРОЕНИЕ ДИЦИАНОДИБРОМОАУРАТА МЕТИЛТРИФЕНИЛФОСФОНИЯ [Ph₃PCH₃][Au(CN)₂Br₂]

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По реакции дицианодибромоаурата калия с бромидом метилтрифенилфосфония в водном растворе синтезирован и структурно охарактеризован дицианодибромоаурат метилтрифенилфосфония (1) [Ph₃PMe]⁺[Au(CN)₂Br₂]⁻. Комплекс представляет собой устойчивое на воздухе кристаллическое вещество желтого цвета с четкой температурой плавления. Строение соединения было подтверждено методами ИК спектроскопии, спектроскопии ЯМР и рентгеноструктурного анализа. В ИК-спектре соединения при 2220 см⁻¹ обнаружена интенсивная полоса поглощения, соответствующая валентным колебаниям цианогрупп. Полоса поглощения деформационных колебаний связей P–C_{Ph} в ИК спектре находится при 1438 см⁻¹. В записанных спектрах ¹H, ¹³C и ³¹P ЯМР наблюдаются сигналы по количеству, значению химических сдвигов и интегральной интенсивности непротиворечащие предложенной структуре комплекса. РСА кристалла 1 проведен на дифрактометре D8 QUEST фирмы Bruker (MoK α -излучение, λ = 0,71073 Å, графитовый монохроматор). [C₂₁H₁₈AuBr₂N₂P, M = 686,13, сингония триклинная, пространственная группа P-1, a = 8,802(5), b = 8,989(5), c = 15,233(11) Å, V = 1143,8(13) Å³, Z = 2, μ = 10,002 мм⁻¹, F(000) = 644, размер кристалла 0,41×0,30×0,22 мм]. По данным РСА в кристалле соединения 1 присутствуют два типа центросимметричных кристаллографически независимых мономерных дицианодибромоауратных анионов и катионы метилтрифенилфосфония. Катионы имеют искаженную тетраэдрическую конфигурацию: углы CPC 108,8(2)–110,0(2)°, расстояния P–C 1,791(5)–1,800(5) Å. В анионах [Au(CN)₂Br₂]⁻ все транс-углы CAuC и BrAuBr равны 180,0°. Расстояния Au–C в анионах отличаются друг от друга и составляют 2,040(7), 2,024(1), 1,991(2) Å. Данные значения близки к сумме ковалентных радиусов атомов (2,03 Å). Длины связей Au–Br в дицианодибромоауратных анионах равны 2,4162(14), 2,4591, 2,474(5) Å. Формирование кристаллической структуры происходит за счет образования слабых водородных связей N...H–C между катионами и анионами (2,68, 2,59, 2,38 Å) и Br...H–C (3,03, 3,02 Å). Полные таблицы координат атомов, длин связей и валентных углов депонированы в Кембриджском банке структурных данных.

Ключевые слова: дицианодибромоаурат калия, бромид метилтрифенилфосфония, дицианодибромоаурат метилтрифенилфосфония, рентгеноструктурный анализ

**SYNTHESIS AND STRUCTURE OF METHYLTRIPHENYLPHOSPHONIUM
DICYANODIBROMOAUATE [Ph₃PCH₃] [Au(CN)₂Br₂]**

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Methyltriphenylphosphonium dicyanodibromoaurate (1) [Ph₃PMe]⁺[Au(CN)₂Br₂][−] was synthesized by the reaction of potassium dicyanodibromoaurate with methyltriphenylphosphonium bromide in an aqueous solution and was structurally characterized. The complex is a yellow-colored, air-resistant crystalline substance with a clear melting point. The structure of the compound was established by IR spectroscopy, NMR spectroscopy and X-ray diffraction analysis. An intense absorption band was observed in the IR spectrum of compound at 2220 cm^{−1}, corresponding to the stretching vibrations of cyano groups. The absorption band of the deformation vibrations of the P – C_{Ph} bonds in the IR spectrum is at 1438 cm^{−1}. In the recorded ¹H, ¹³C, and ³¹P NMR spectra, signals are observed for the number, value of chemical shifts and integral intensity that do not contradict the proposed complex structure. The X-ray diffraction analysis of crystal 1 was carried out on a Bruker D8 QUEST diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). [C₂₁H₁₈AuBr₂N₂P, M = 686.13, crystal system triclinic, space group P-1, a = 8.802(5), b = 8.989(5), c = 15.233(11) Å, V = 1143.8(13) Å³, Z = 2, μ = 10.002 mm^{−1}, F(000) = 644, crystal size 0.41×0.30×0.22 mm]. According to the X-ray diffraction analysis (XRDA) data there are two types of centrosymmetric crystallographically independent monomeric dicyanodibromoaurate anions and methyltriphenylphosphonium cations in the crystal of compound MFDDA. The cations have a distorted tetrahedral configuration: the CPC angles equal 108.8(2)°–110.0(2)°, the P–C distances are 1.791(5)–1.800(5) Å. All CAuC and BrAuBr trans-angles are 180.0° in the [Au(CN)₂Br₂][−] anions. The Au–C distances in anions differ from each other and equal 2.040(7), 2.024(1), 1.991(2) Å. These values are close to the sum of the covalent radii of atoms (2.03 Å). The Au-Br bond lengths are equal to 2.4162(14), 2.4591, 2.474(5) Å in dicyanodibromoaurate anions. Formation of the crystal structure occurs due to formation of weak N...H–C hydrogen bonds between cations and anions (2.68, 2.59, 2.38 Å) and Br...H–C (3.03, 3.02 Å). Complete tables of coordinates of atoms, bond lengths and valence angles are deposited at the Cambridge Crystallographic Data Centre.

Key words: potassium dicyanodibromoaurate, methyltriphenylphosphonium bromide, methyltriphenylphosphonium dicyanodibromoaurate, X-ray diffraction analysis

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INTRODUCTION

To date, the ionic complexes of gold in the form of tetrahalogenaurate and dicyanoaurate anions have been studied well [1-7]. The most interesting are the last ones due to their use in the preparation of semiconductor, magnetic and optically active materials [8-14]. In addition, dicyanoaurate complexes are active metabolites of several drugs [15]. It has been shown that $[\text{Au}(\text{CN})_2]^-$ anions can form oligomers with luminescent properties [11, 16-19]. Currently, several cyanide complexes of monovalent gold [20, 21] and cyanohalide complexes of trivalent gold are known [22-24]. It should be noted that the $[\text{Kat}]^+[\text{Au}(\text{CN})_2\text{Hal}_2]^-$ complexes with organometallic cations have not been studied.

EXPERIMENTAL PART

The IR spectrum of complexes methyltriphenylphosphonium dicyanodibromoaurate (1) was recorded on a Shimadzu IR Affinity-1S IR-Fourier spectrometer in the region of 4000-400 cm^{-1} using the KBr pellet.

The ^1H (600 MHz), ^{13}C (151 MHz), ^{31}P (243 MHz) NMR spectra were recorded for DMSO- d_6 solutions of compounds on a Bruker AVANCE NEO NMR-spectrometer. Solvent signals were used as the internal standard for the ^1H and ^{13}C NMR spectra, and the external standard H_3PO_4 was used for the ^{31}P NMR spectra.

X-ray diffraction study of single crystal 1 was accomplished on a Bruker D8 QUEST diffractometer (Mo- K_α radiation, $\lambda = 0.71073 \text{ \AA}$, graphite monochromator) at 293 K. Collection, editing of data and refinement of the unit cell parameters, as well as accounting for absorption, were carried out using the SMART and SAINT-Plus programs [25]. All calculations were performed using the SHELXTL/PC [26], OLEX2 [27] software. The structure was solved by the direct method and refined by the method of least squares in the anisotropic approximation for non-hydrogen atoms. Selected crystallographic data and refinement results for the structure of complex 1 are given in Table 1, and selected bond lengths and bond angles are listed in Table 2.

Complete tables of coordinates of atoms, bond lengths and valence angles are deposited at the Cambridge Crystallographic Data Centre (No. 1896043 (1); deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk>).

Synthesis of methyltriphenylphosphonium dicyanodibromoaurate $[\text{Ph}_3\text{PCH}_3]^+[\text{Au}(\text{CN})_2\text{Br}_2]^-$ (1). To a solution of 80 mg (0.223 mmol) of methyltriphenylphosphonium bromide in 10 ml of water a solution of 100 mg (0.223 mmol) of potassium dicyanodibromoaurate in 4 ml of water was added, stirred and kept at 20 °C for 14 h. Water was removed, the residue was washed with acetonitrile (2×4 ml). Upon slow

evaporation of the solvent, formation of yellow crystals was observed. 145 mg (95%) of the 1 complex with mp 150 °C was obtained.

Table 1
Crystallographic data, parameters of X-ray diffraction experiment, and refinement details for the structure of complex 1

Таблица 1. Кристаллографические данные и результаты уточнения структуры 1

Parameter	Value
Formula weight	686.13
Crystal system	Triclinic
Space group	$P\bar{1}$
$a, \text{ \AA}$	8.802(5)
$b, \text{ \AA}$	8.989(5)
$c, \text{ \AA}$	15.233(11)
$\alpha, ^\circ$	102.61(2)
$\beta, ^\circ$	90.46(4)
$\gamma, ^\circ$	103.023(19)
$V, \text{ \AA}^3$	1143.8(13)
Z	2
$\rho_{\text{calc.}}, \text{ g/cm}^3$	1.992
$\mu, \text{ mm}^{-1}$	10.002
$F(000)$	644
Crystal size, mm	0.41×0.30×0.22
2 θ range, $^\circ$	6.02–52.72
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-19 \leq l \leq 19$
Measured reflections	42008
Independent reflections	4653 ($R_{\text{int}} = 0.0423$)
Reflections with $I > 2\sigma(I)$	3562
Refinement variables	276
$GOOF$	1.057
Final R indexes $F^2 > 2\sigma(F^2)$	$R_1 = 0.0276$, $wR_2 = 0.0618$
Final R indexes [all data]	$R_1 = 0.0424$, $wR_2 = 0.0675$
Largest diff. peak/hole, $e/\text{ \AA}^3$	0.428/–0.828

IR spectrum ($\nu, \text{ cm}^{-1}$): 3061, 2991, 2916, 2360, 2220, 2167, 1587, 1487, 1438, 1419, 1398, 1340, 1325, 1311, 1193, 1163, 1116, 1028, 997, 979, 935, 898, 837, 786, 752, 740, 719, 686, 507, 472, 449, 430.

^1H NMR (DMSO- d_6 , 600 MHz): δ 3.16 (d, 3H, $J_{\text{C-P}} = 14.5 \text{ Hz}$, $-\text{CH}_3$), 7.77 (m, 12H, arom. p -H), 7.90 (m, 3H, arom. o - and m -H).

^{13}C NMR (DMSO- d_6 , 151 MHz): δ 7.26 (d, C-7, $J = 55.5 \text{ Hz}$), 109.46 (CN), 119.85 (d, C_i , $J = 88.3 \text{ Hz}$), 130.09 (d, C_o , $J = 12.64 \text{ Hz}$), 133.23 (d, C_m , $J = 10.76 \text{ Hz}$), 134.82 (C_p).

^{31}P NMR (DMSO- d_6 , 243 MHz): δ 22.65.

For $\text{C}_{21}\text{H}_{18}\text{AuN}_2\text{PBr}_2$, anal. calcd. (%): C, 36.63, H, 2.71.

Found (%): C, 36.76; H, 2.65.

Table 2
Selected bond lengths (d) and bond angles (ω) in the structure of complex 1

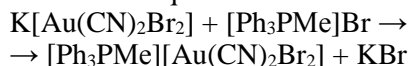
Таблица 2. Основные длины связей и валентные углы в структуре 1

Bond	d, Å	Angle	ω, deg
Au(1)–C(8)	2.040(7)	C(8)Au(1)C(8)	180
Au(1)–Br(1)	2.4162(14)	C(8)Au(1)Br(1)	89.96(16)
Au(2A)–C(9A)	2.024(13)	C(8)Au(1)Br(1)	90.04(16)
Au(2A)–Br(2A)	2.4591(13)	Br(1)Au(1)Br(1)	180
Au(2B)–C(9B)	1.991(16)	C(9A)Au(2A)C(9A)	180
Au(2B)–Br(2B)	2.474(5)	C(9A)Au(2A)Br(2A)	92.4(6)
P(1)–C(7)	1.791(5)	C(9A)Au(2A)Br(2A)	87.6(6)
P(1)–C(21)	1.801(4)	C(7)P(1)C(1)	109.6(2)
P(1)–C(11)	1.800(4)	C(7)P(1)C(11)	109.5(2)
P(1)–C(1)	1.798(4)	C(1)P(1)C(11)	109.21(19)
C(8)–N(1)	1.013(6)	C(7)P(1)C(21)	109.7(2)
C(9A)–N(2A)	1.077(15)	C(1)P(1)C(21)	108.8(2)
C(9B)–N(2B)	1.038(17)	C(11)P(1)C(21)	110.0(2)

RESULTS AND DISCUSSION

In this work, for the first time methyltriphenylphosphonium dicyanodibromaurate $[\text{Ph}_3\text{PMe}]^+[\text{Au}(\text{CN})_2\text{Br}_2]^-$ (1) was synthesized and structurally characterized.

1 complex has been synthesized from potassium dicyanodibromaurate and methyltriphenylphosphonium bromide in an aqueous solution:



Yellow, air-resistant crystals were obtained after evaporation of water, drying of the solid residue and recrystallization of it from acetonitrile.

The absorption region of cyano groups in the IR spectra of organic and inorganic compounds is in a rather narrow range of values: 2200–2000 cm^{-1} . This circumstance indicates that there is no strong influence of the environment on vibrations of these bonds [28]. Therefore, cyanides are easily identified by absorption in the specified area. Indeed, an intense absorption band at 2220 cm^{-1} was detected in the IR spectrum of compound 1. The absorption band of the deformation vibrations of the P–C_{Ph} bonds in the spectrum of compound 1 is at 1438 cm^{-1} , which corresponds to the absorption region of 1450–1435 cm^{-1} , given in [28]. In the ^1H NMR spectrum, *p*-proton multiplets characteristic of the phenyl ring are observed at 7.90 ppm, *m*- and *o*-protons at 7.77 ppm and at 3.16 ppm a doublet of the methyl group with a characteristic splitting on the

phosphorus atom with SSCC 14.5 Hz. In the ^{13}C NMR spectrum all signals except the signals of carbon at 109.46 (carbon of the cyano group) and 134.82 ppm (carbon C_p of the aromatic ring) are observed in the form of doublets with the corresponding constants due to the spin-spin interaction with the phosphorus atom. Due to the influence of the phosphorus atom, an insignificant upfield shift of carbon signals is also observed, and the signals of the methyl group and the *ipso*-carbon of the phenyl ring are directly related to it. A single signal of a phosphorus atom is recorded in the ^{31}P NMR spectrum.

According to the XRDA data, there are two types of centrosymmetric crystallographically independent monomeric dicyanodibromaurate anions and methyltriphenylphosphonium cations in crystal 1 (Figure).

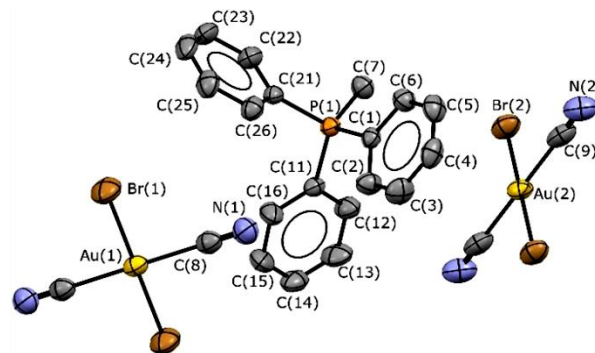


Fig. Structure of complex 1
Рис. Строение комплекса 1

The tetrahedral coordination of the phosphorus atom in the methyltriphenylphosphonium cation is slightly distorted: the CPC angles are close to the theoretical value and are 108.8(2)°, 109.2(2)°, 109.5(2)°, 109.6(2)°, 109.7(2)°, 110.0(2)°; P–C bond lengths (1.791 (5), 1.800 (5), 1.800 (4), 1.798 (5) Å) are close to each other and do not depend on the nature of the substituent. The square $[\text{Au}(\text{CN})_2\text{Br}_2]^-$ anions do not deviate from the flat configuration, the CAuC angles are equal to 180°. One of the anions is statistically disordered in two positions. The central Au atom in it coincides in positions that are rotated in relation to each other by 95°. The refined ratio of the position contributions to the disordered fragment is 0.68/0.32. The Au(1)–C(8), Au(2A)–C(9A), Au(2B)–C(9B) distances in anions are different from each other and are: 2.040(7), 2.024(1), 1.991(2) Å. These values are close to the sum of covalent radii of the atoms (2.03 Å [29]). The Au–Br bond lengths in dicyanodibromaurate anions are equal to 2.4162(14), 2.4591, 2.474(5) Å.

The structural organization of crystals is due to N...H–C weak hydrogen bonds between cations and anions (2.68, 2.59, 2.38 Å) and Br...H–C (3.03, 3.02 Å).

CONCLUSION

Thus, the gold complex obtained from methyltriphenylphosphonium bromide and potassium dicyanodibromaurate in water is crystallized in the ionic

structure with monomeric dicyanodibromaurate anions.

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